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**NRL Report 5874**

# HALL COEFFICIENT OF SUPERCONDUCTING AND NORMAL Nb-25% Zr

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## ABSTRACT

Hall-coefficient measurements were made on cold-rolled Nb-25% Zr in the zero-resistance mixed state at 4.2°K and in the normal state at 4.2°K, 77°K, and 317°K. With sample current densities from  $2 \times 10^3$  to  $1 \times 10^4$  amp/cm<sup>2</sup> in fields of 1 and 9 kilogauss, no Hall voltage for the superconducting sample could be observed with equipment capable of detecting voltages as small as  $10^{-9}$  volt. An upper limit of the superconducting Hall coefficient is therefore calculated to be  $1 \times 10^{-15}$  m<sup>3</sup>/amp-sec. The values of the Hall coefficient for Nb-25% Zr in the normal state are found to be  $1.14 \times 10^{-10}$ ,  $1.05 \times 10^{-10}$ , and  $0.84 \times 10^{-10}$  m<sup>3</sup>/amp-sec at 4.2°K, 77°K, and 317°K, respectively.

## PROBLEM STATUS

This is an interim report on one phase of the problem; work on this and other phases is continuing.

## AUTHORIZATION

NRL Problem M01-10  
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## HALL COEFFICIENT OF SUPERCONDUCTING AND NORMAL Nb-25% Zr

### INTRODUCTION

Hall-coefficient data have proven quite useful in evaluating the merits of electron-transport theory, and it would be expected that the detection of a Hall effect in superconducting material would be equally useful in the study of the superconducting state. Theoretical arguments have been proposed (1-3) for the nonexistence of a superconducting Hall effect, and in fact all previous experiments have failed to detect a Hall effect in a superconductor. However, these theoretical conclusions have been primarily based upon properties of soft superconducting metals. Likewise, experiments were performed exclusively on elemental superconductors either in the intermediate state or in the pure superconducting state (4-6). Recently, hard superconducting alloys have been discovered which exhibit a type of superconducting state, the mixed state (7,8), which is quite different from that of soft superconductors in either the pure or intermediate superconducting state.

From a practical point of view, the extremely large critical fields and currents of these new superconducting alloys would enable measurements of greatly increased sensitivity to be made, and therefore, a detectable voltage could be observed even if the Hall coefficient was orders of magnitude smaller than the upper limit given by previous investigators. In addition, the radically different properties of hard superconducting alloys, such as negative surface energies, short electronic mean free paths, large penetration depths, and short coherence lengths, were not considered in the theoretical arguments presented for the nonexistence of a superconducting Hall effect. Consequently, it is relevant to inquire into the existence of a superconducting Hall effect for these materials.

In discussing the existence of a superconducting Hall effect, it is necessary to establish the presence of both a current density and a magnetic field in the superconducting region. Even in a soft superconductors exhibiting a Meissner effect this condition is met because we can conclude from  $\mathbf{j} = \text{curl } \mathbf{H}$  that the currents will be found in regions where  $\text{curl } \mathbf{H}$ , and consequently  $\mathbf{B}$ , is different from zero. Thus, the above conditions necessary for a Hall voltage will always exist. In the case of the newly discovered hard superconductors, this condition is again obviously met. In fact, measurements of the magnetic properties of these hard superconducting alloys in the mixed state would indicate almost complete magnetic flux penetration. (9,10).

Theoretical arguments for the nonexistence of a superconducting Hall effect have been proposed by London (1), Pippard (2), and Bardeen (3). Since their work predated the discovery of the hard superconducting alloys, they were primarily concerned with the case of the soft superconductor. The bases for the discussions of London and Pippard have been criticized by Lewis (11) and will not be reproduced here. On the other hand, Bardeen has stated that since the wave functions of superconducting electrons extend over distances large compared to the penetration depth, one could not localize superconducting electrons within the penetration depth. As a consequence, one cannot localize the force due to a magnetic field, as in the case for a classical stream of particles, and no Hall effect would result. However, in a hard superconducting alloy, a filamentary structure has been proposed in which the filamentary diameters are smaller than the penetration depth (10,12). As a result, Bardeen's conclusions do not appear to apply.

## SAMPLE PREPARATION AND MEASURING APPARATUS

The hard superconducting alloy chosen for the present experiment was Nb-25% Zr, because in addition to remaining superconducting in the presence of large fields and currents, it is also easily fabricated. The alloy was made by arc melting a cylindrical compact of Nb and Zr, using a tungsten electrode in a helium atmosphere. To obtain homogeneity, the material was turned over and remelted several times in a water-cooled copper crucible. The ingot was completely enclosed in titanium and hot-rolled to a thickness of 0.05 in. The titanium was then removed by grinding, and the alloy was vacuum annealed and cold-rolled to a thickness of 0.003 in. A sample  $7.0 \times 0.7$  cm with 0.6-cm-long Hall probes (Fig. 1) was cut from this material. (A spectroanalysis of the ends of this sample is given in Table 1.) The current and potential leads were spot welded to the sample. Copper plates (1/8 in. thick) which were electrically insulated from the sample with 1-mil-thick Mylar film were placed on the faces of the sample. These plates greatly reduced the noise encountered when the sample was at 4.2°K in the normal state. A flux coil, which was calibrated against a nuclear magnetic resonance gaussmeter, was mounted in one of the copper plates. The sample was then screwed to a bakelite frame, which held it in place at the bottom of a helium magnet dewar.

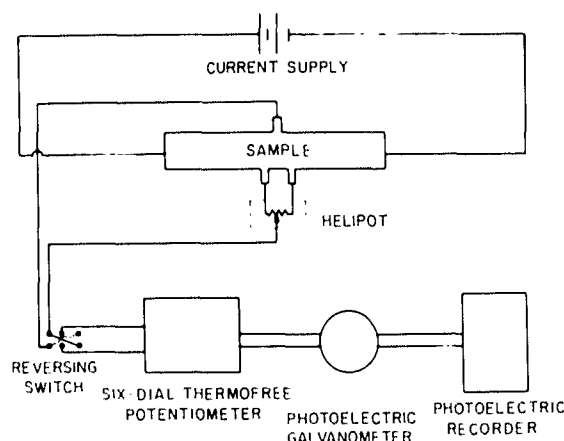


Fig. 1 - Block diagram of circuit used in the measurement of the Hall voltage

The transverse Hall voltage was measured using a three-probe direct current method (Fig. 1). The three-probe arrangement is convenient for measurements in the normal state and also for determining whether or not there is resistance between the probes in the mixed state. The current was supplied to the sample by a 4-volt, 1100-ampere-hour battery, and the transverse voltage was measured with a six-dial thermo-free potentiometer which employed a photoelectric galvanometer. With this arrangement a voltage as low as  $10^{-9}$  volt could be measured. The magnetic field was measured with the flux coil. The total variation in the field over a circle 2 in. in diameter was approximately 0.1 per cent for a 5-kilogauss field in the 2-1/4-in. gap used throughout the experiment.

## EXPERIMENTAL PROCEDURE

In an attempt to measure a Hall voltage while the sample was in a zero-resistance mixed state, currents from 1 to 50 amperes in fields of 1 and 9 kilogauss were used. The voltage between the probes was recorded as a function of time. The magnetic field (or the sample current) was reversed, and any change in the transverse voltage was noted. Then the magnetic field (or the sample current) was again reversed to see if there had been any drifting of the original voltage. This procedure was repeated several times. The

Table 1  
Sample Composition

Material	Amount in Sample (atomic percent)	Type of Analysis
Nb	75.8±0.2	X-ray spectrochemical
Zr	24.2±0.2	X-ray spectrochemical
Ta	0.1-1	Optical spectrochemical
Hf	0.1-1	Optical spectrochemical
O <sub>2</sub>	0.175	Vacuum fusion
N <sub>2</sub>	0.045	Vacuum fusion
Ti	0.001-0.01	Optical spectrochemical
Si	0.001-0.01	Optical spectrochemical
Cu	0.001-0.01	Optical spectrochemical
Fe	0.001-0.01	Optical spectrochemical
Al	0.0001-0.001	Optical spectrochemical
Mg	0.0001-0.001	Optical spectrochemical

magnetic-field reversals were made for both positive and negative directions of the sample current, and the current reversals were made for both positive and negative directions of the magnetic field. Both field and current reversals were also made for direct and for reversed leads to the Hall probes.

Since magnetic flux can be trapped in hard superconductors, such as Nb-25% Zr, the sample was cooled in fields of 1 and 9 kilogauss to see if this trapping would affect the Hall voltage. Flux was also trapped by increasing the current and field until the sample became normal and by then reducing the current until the sample again became superconducting. After each trapping, the above procedure for measuring the Hall effect was again repeated.

Measurements of the Hall coefficient in the normal state in the vicinity of liquid helium temperatures were made as follows. To transform the sample into the normal state, a sample current exceeding 50 amperes was turned on for a fraction of a second and was then reduced to a value of about 17 amperes. Above 17 amperes the noise in the transverse voltage increased significantly. This noise is believed to have been caused by thermal fluctuations produced by joule heating. Below approximately 14 amperes the noise also increased. Since at the same time the sample current fluctuated, this noise is believed to have been caused by changing sample resistance. Between 10 and 12 amperes, the sample became superconducting.

Because of the vigorous boiling resulting from the joule heating, measurements were made as soon as possible after the current was turned on. Each potential measurement was made by reversing the field several times and determining the change in the transverse voltage. Measurements were made in fields ranging from 1 to 9 kilogauss.

The potential measurements at 77° K and 317° K were made not only by a field-reversal technique but also by an incremental method (13). In the incremental method, the change in transverse voltage was measured upon changing the magnetic field back and forth between a fixed maximum field and some lower field. The fixed field value was 9 kilogauss, and the

other was varied in order to change the size of the field increment. The measurements (using both techniques) were made for both positive and negative sample-current directions. The sample current was measured after each potential measurement. Field measurements were made after the equipment had warmed up to room temperature.

## RESULTS

In all cases investigated (different currents, fields, trapped flux, etc.) when the sample was superconducting, no Hall voltage could be detected. The sensitivity and the noise level were each approximately  $1 \times 10^{-9}$  volt; these values are comparable with those that could be obtained by shorting the potentiometer input. This low noise level is believed to result from the absence of both joule heating and thermoelectric effects. There was, however, an indication on the recorder of a voltage change when the sample current was reversed. The average magnitude of this voltage for 282 reversals was  $5 \times 10^{-9}$  volt, with an average deviation  $4 \times 10^{-9}$  volt. The largest voltage change noted was  $15 \times 10^{-9}$  volt. The direction of this voltage change depended upon the direction of the current reversal, but the magnitude and direction of the change did not depend upon the magnitude or direction of the magnetic field, the history of the sample, or the direction of the Hall-probe leads. It was therefore concluded that this voltage was not a Hall voltage.

The upper limit of the superconducting Hall coefficient was determined to be  $1 \times 10^{-15}$  m<sup>3</sup>/amp-sec. This upper limit for the Hall coefficient is less than  $10^{-5}$  times the measured value in the normal state at the same temperature and less than  $10^{-3}$  times the upper limit determined by previous investigators (4-6) (Table 2).

Table 2  
Hall Coefficients for Superconducting Materials

Material	Hall Coefficient (m <sup>3</sup> /amp-sec)	Temperature (°K)	State of Sample	Observer
Pb	$< 6 \times 10^{-12}$	2.8	Intermediate	Kamerlingh-Onnes and Hof (4)
V	$< 15 \times 10^{-12}$	1.5	Superconducting	Lewis (5)
Hg	$< 15 \times 10^{-12}$	2	Superconducting	Jaggi and Somerhalder (6)
Pb	$< 2 \times 10^{-12}$	2	Superconducting	"
Sn	$< 16 \times 10^{-12}$	2	Superconducting	"
Nb-25% Zr	$< 1 \times 10^{-15}$	4.2	Mixed	Present investigation
Nb-25% Zr	$+1.14 \times 10^{-10}$	4.2*	Normal	"
Nb-25% Zr	$+1.05 \times 10^{-10}$	77*	Normal	"
Nb-25% Zr	$+0.84 \times 10^{-10}$	311*	Normal	"

\* See the end of the Results section for a discussion of temperature error in the normal state



The upper limit of the superconducting Hall coefficient was computed on the basis of a uniform sample current density throughout the sample. If, however, the upper bound of the Hall coefficient is computed on the basis of the current being carried by superconducting filaments, the upper bound will be reduced. For example, with the assumption of a uniform field and uniform current densities in the filaments (i.e., the filaments are much smaller than the penetration depth) and an isotropic distribution of the filaments, the upper bound of the Hall coefficient will be reduced by a factor of about ten for the case of a specimen which is 1-percent superconducting. The volume of the specimen which is superconducting can be estimated from heat-capacity data (10).

The data taken when the sample was in the normal state are plotted in Fig. 2, and the results of both superconducting and normal measurements are shown in Table 2 along with the superconducting results of previous investigators. The Hall coefficient in the normal state was computed by calculating the Hall coefficient for each field point and averaging the results.

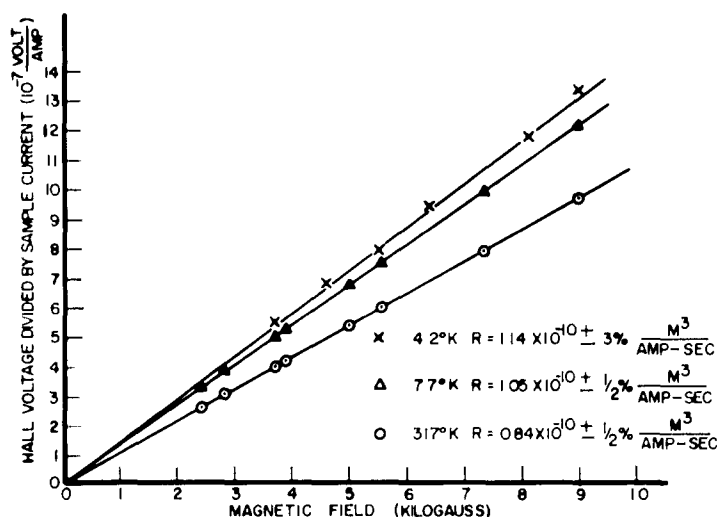


Fig. 2 - Hall voltage per unit sample current as a function of magnetic field for Nb-25 percent Zr at 4.2°K, 77°K, and 317°K

The largest source of error (about 3 percent) occurred in the measurement of the sample thickness. The magnetic field and the sample current could both be measured to an accuracy of better than 1 percent. The Hall potential at 77°K and 317°K could be measured to better than 1 percent and at 4.2°K could be measured to about 4 percent. The maximum absolute error in the Hall coefficient is estimated to be less than 6 percent at 77°K and 317°K and less than 10 percent at 4.2°K; however, the average deviation (for the Hall coefficients at different fields) was 1/2 percent for the sample at 77°K and 317°K and 3 percent at 4.2°K. Since there were no systematic deviations with field, it is concluded that the Hall coefficient in the normal state is independent of the magnetic field. The larger average deviation at 4.2°K was caused by the large noise, which was about  $10^{-7}$  volt/amp at 17 amperes. The measurement at 9 kilogauss with different currents indicated that the Hall coefficient is also independent of current.

A difference of approximately 40 amp was observed between the value of the current necessary to transform the sample into the normal state and the value of the current at which the sample again became superconducting. This fact, along with a consideration of the sample arrangement, indicates that the temperature of the sample may have been significantly above that measured at the copper plate. A calculation of the upper limit of this temperature difference resulted in a value of 20°K. However, the Hall coefficient at the higher temperature should be within 2 percent of that at 4.2°K, since the three measured Hall coefficients show a temperature dependence of about 0.1 percent per degree. A similar calculation at 77°K and 317°K indicated that the change in the Hall coefficient was less than 1/2 percent.

#### DISCUSSION

These measurements indicate that the Hall coefficient of hard superconductors in the zero-resistance mixed state is less than  $1 \times 10^{-15}$  m<sup>3</sup>/amp-sec. However, since the sample was in the mixed state, the question arises: even if a Hall effect does exist in the superconducting regions, can it be detected by using the method employed in the present experiment? The observation of this Hall voltage in the specimen requires that the electrons be mobile in the direction of the expected Hall field. The only place at which mobility might be questioned is at the superconducting normal interface. However, other investigations have shown that it is possible for the resistance of the mixed state to be nonzero and less than the normal state (14); this indicates that the electrons can traverse the superconducting-normal interface. It is therefore concluded that the null result obtained probably implies that a dc Hall effect does not exist in the superconducting regions.

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